Exceptional Chloride resistance of LC3

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With acknowledgements to contributions from:

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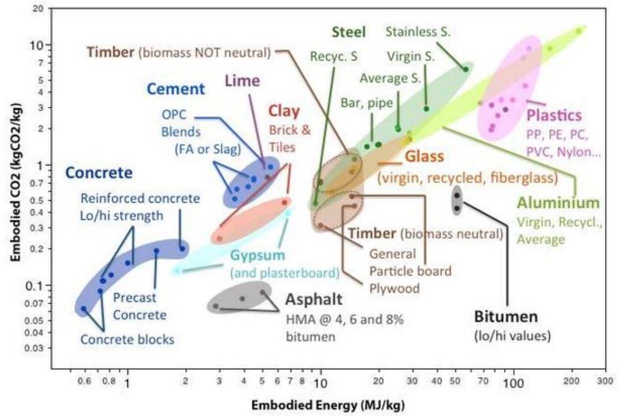
Dr William Wilson

Dr Franco Zunino

LABORATORY OF CONSTRUCTION MATERIALS

Need to reduce CO_2 emissions

- No alternative to concrete,
- No practical alternative
  to Portland cement clinker at scale,
- Best way to reduce CO_2 emissions fast and at scale
  is increase use of blended cements
- BUT final product is concrete:
- Need to take concrete performance into account
  - Lower clinker factor not always better
- How to ensure we have a low permeability,
  durable concrete
  with adequate strength
  at minimal CO_2?



Eco-efficient cements:
Potential economically viable
solutions for a low-CO_2
cement-based materials industry

Reduction needed through the value chain

Reduce CO_2 from clinker production → Reduce clinker in cement → Reduce cement in concrete → Reduce concrete in building → More efficient (re)use of buildings

- SCMs

- Aggregate grading
- Good admixtures
- Use filler

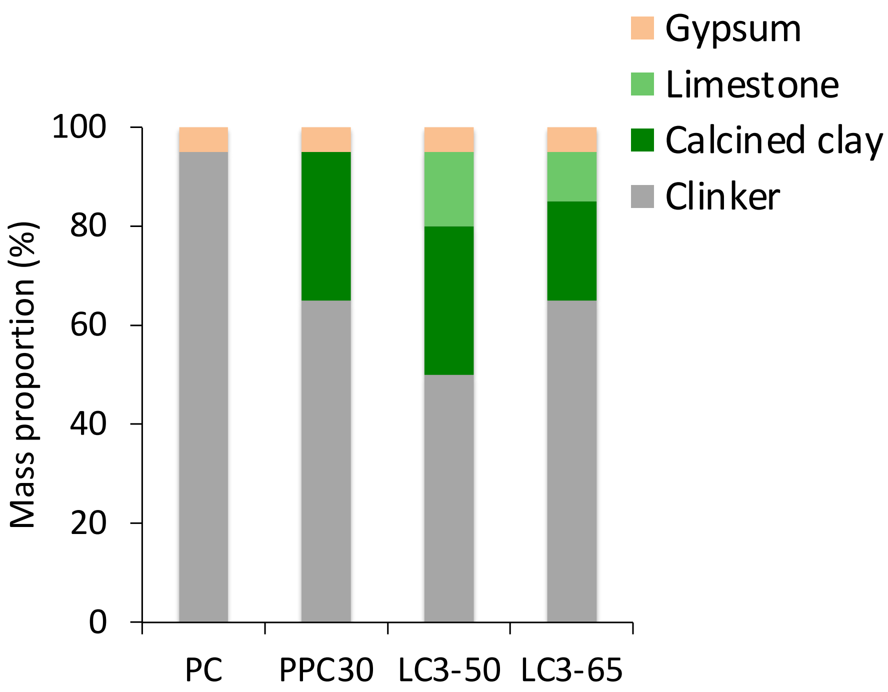
Availability of SCMs

LC^3 concept

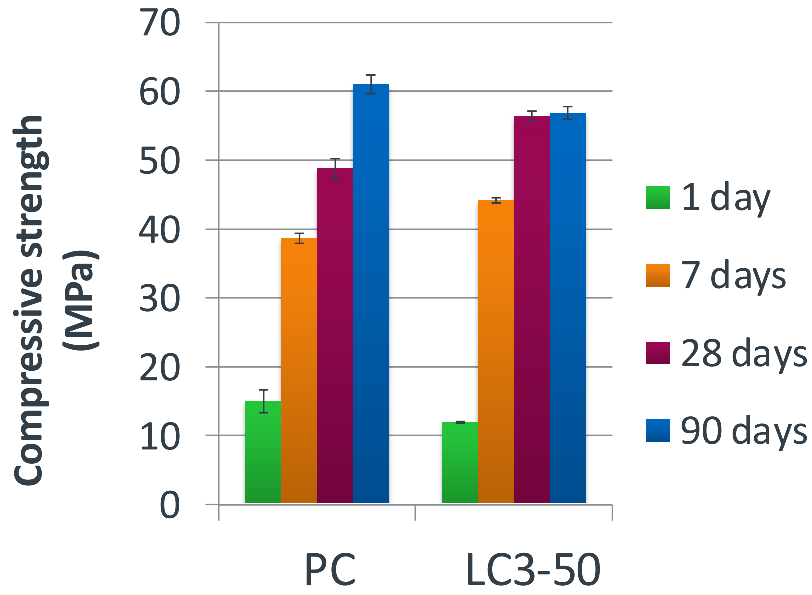
- Blended with SCMs will be best solution for sustainable cements for foreseeable future
- **Only material really potentially available in viable quantities is calcined clay**.
- **Synergetic reaction** of calcined clay and limestone allows high levels of substitution:

Limestone
Calcined
Clay
Cement
LC^3

What is LC³



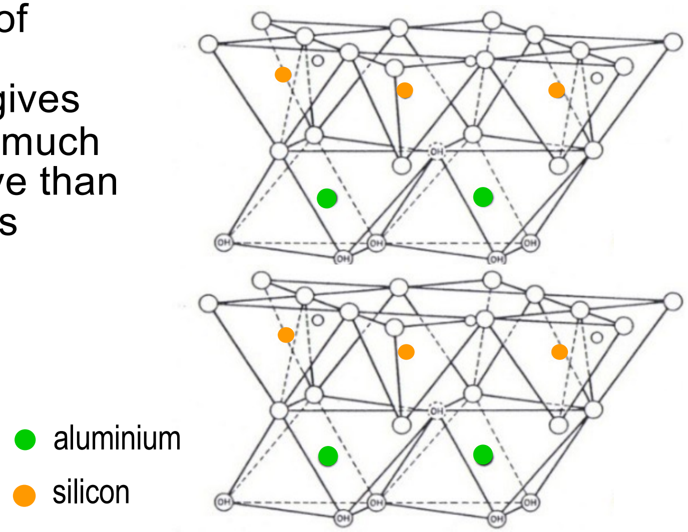
LC³ is a family of cements, the figure refers to the **clinker** content

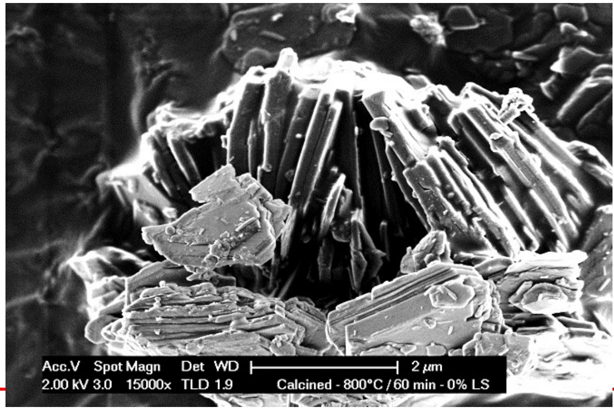


- 50% less clinker
- 40% less CO_2
- Similar strength
- Better chloride resistance
- Resistant to alkali silica reaction

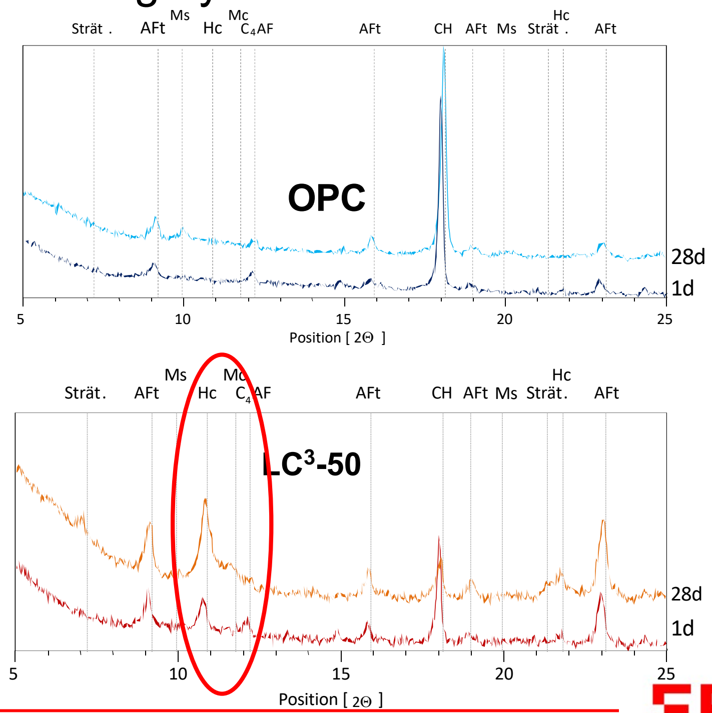
Why can we get such high replacement levels

- Calcination of kaolinite at **700-850°C** gives metakaolin: much more reactive than glassy SCMs





» **Synergetic reaction** of Alumina in metakaolin with limestone to give space filling hydrates



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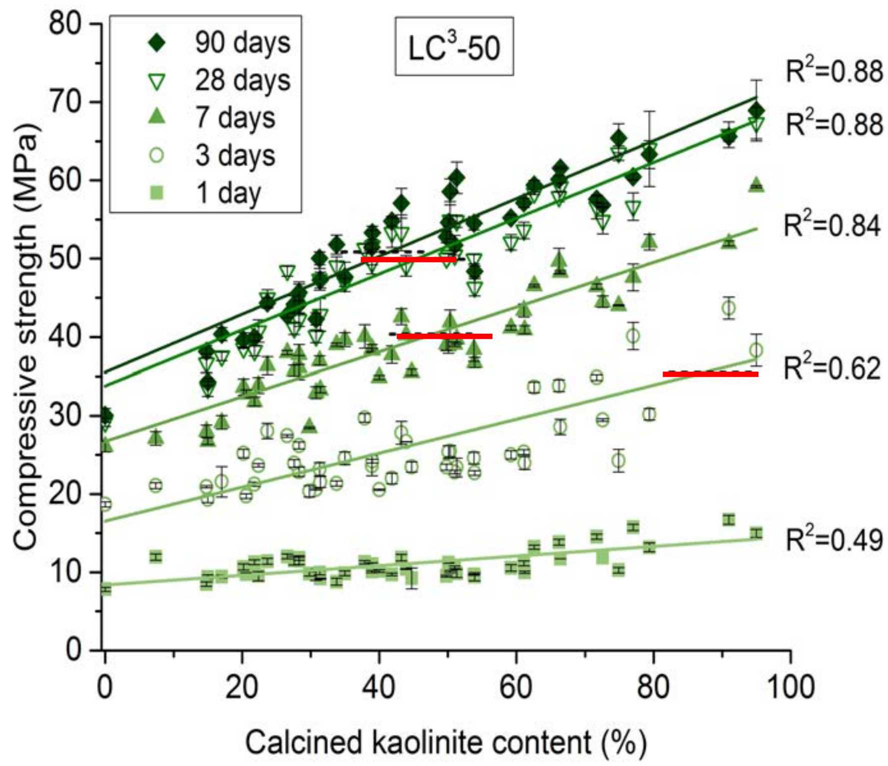
Benchmark test of clay strength

- Compressive strength EN 196-1 at 1, 3, 7, 28, 90 d
- Linear increase of strength with the MK content of calcined clays
- Similar strength to PC for blends containing 40% of calcined kaolinite from 7d onwards
- At 28 and 90 days, little additional benefit >60%
- Minor impacts of fineness, specific surface and secondary phases



Calcined kaolinite content overwhelming parameter

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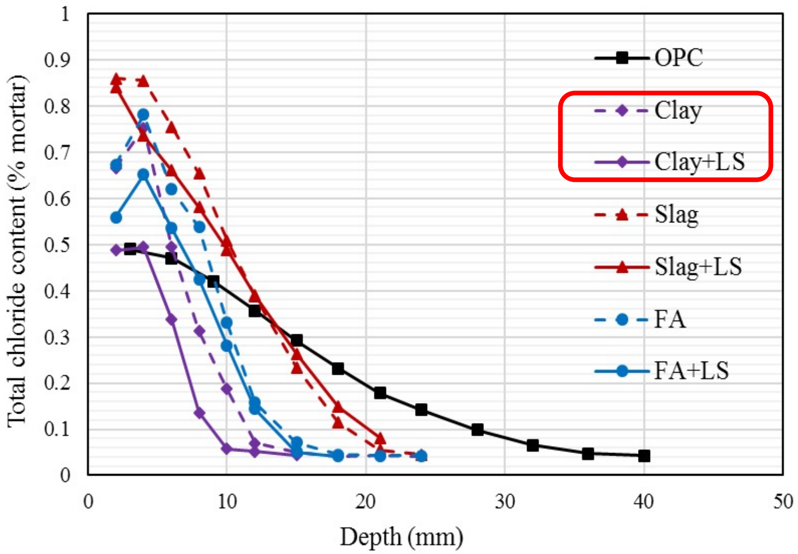
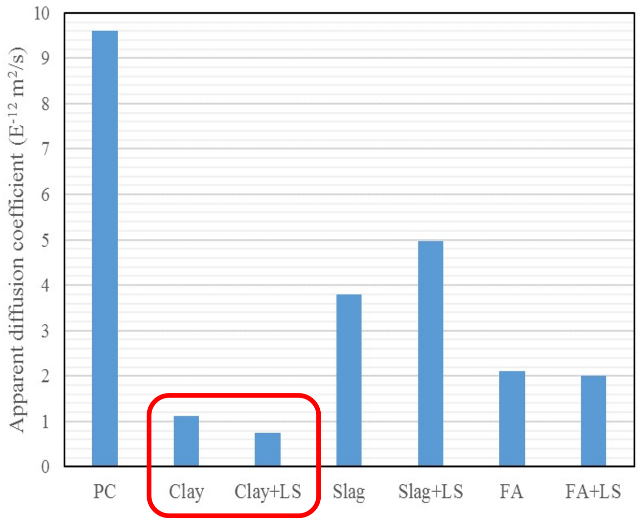
Chloride ingress & migration

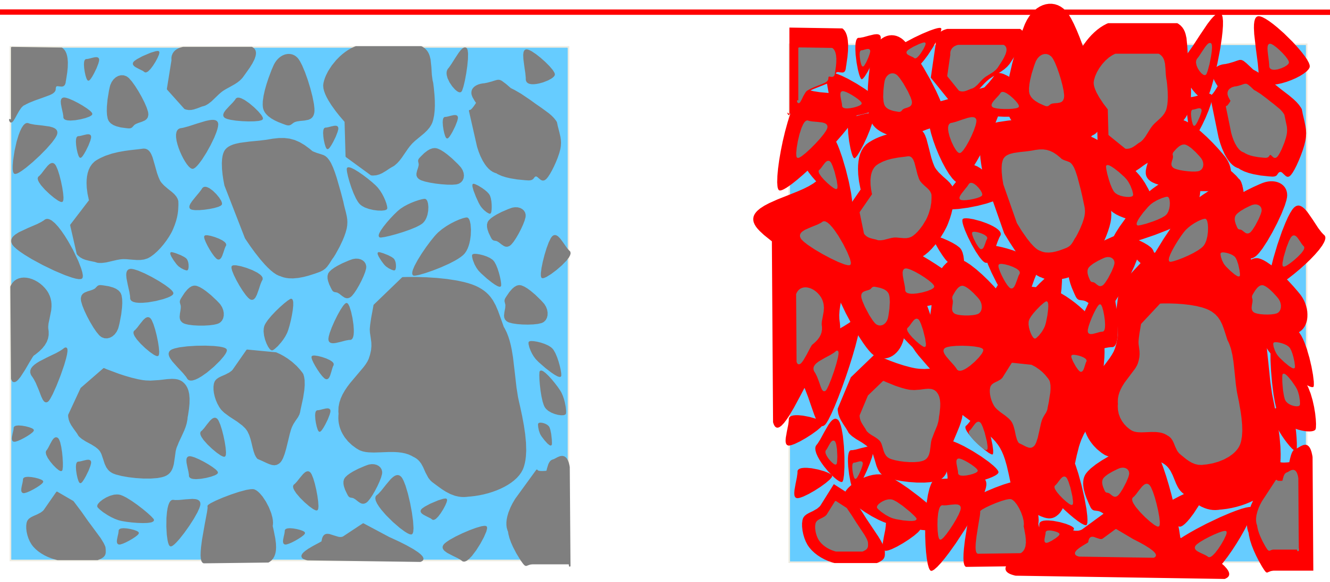


Cl profiles for different binders



Apparent diffusion coeffs.

Hydration is about space filling:



This is a combination of:

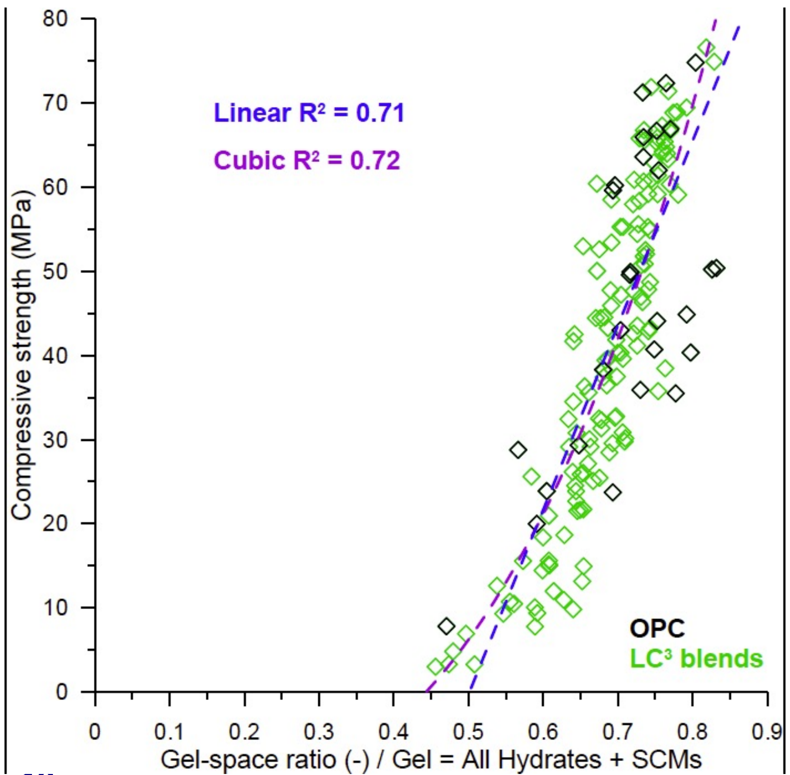
Reactive materials

Water / Cement ratio

Relationship of pore filling to properties

Mechanical

- Strength and other mechanical properties correlate with porosity in a fairly straightforward way.



Relationship to
"gel-space ratio" = f(1/porosity)

A lot of scatter in part due to experimental measurement, but clearly shows space filling / porosity dominates

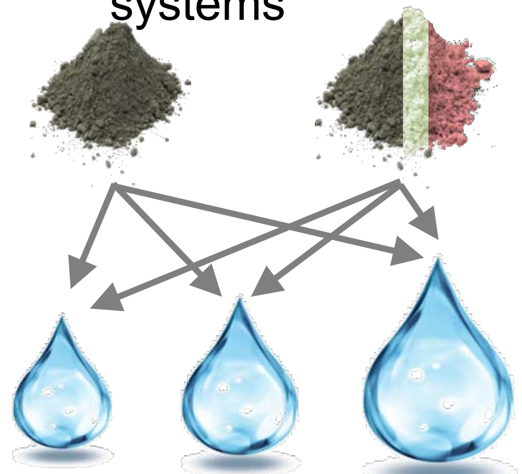
Chloride ingress more complex:

General approach

Decouple variables → Consider "simple" and diversified systems → Use/adapt methods for saturated pastes

OPC Systems

100% CEM I
(Holcim)



LC3-50 Systems

50% CEM I
+ 30% Calcined clay (Buhj, 45%)
+ 15% Limestone (Durcal5)
+ 2 % Gypsum

Sample preparation

Vacuum mixing

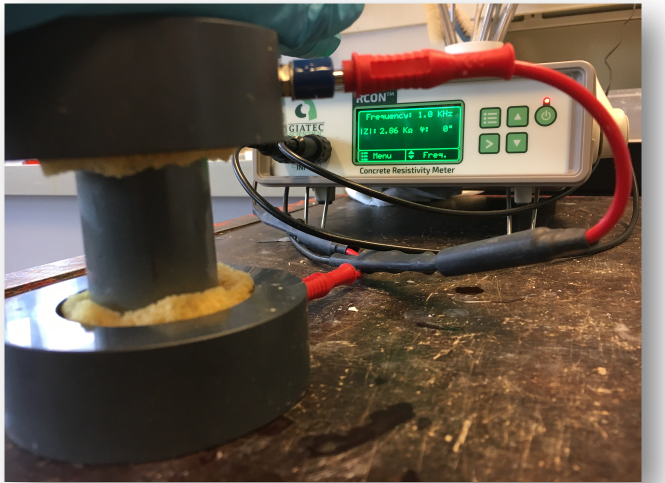
Water-curing for 28d
(in "pore solution")

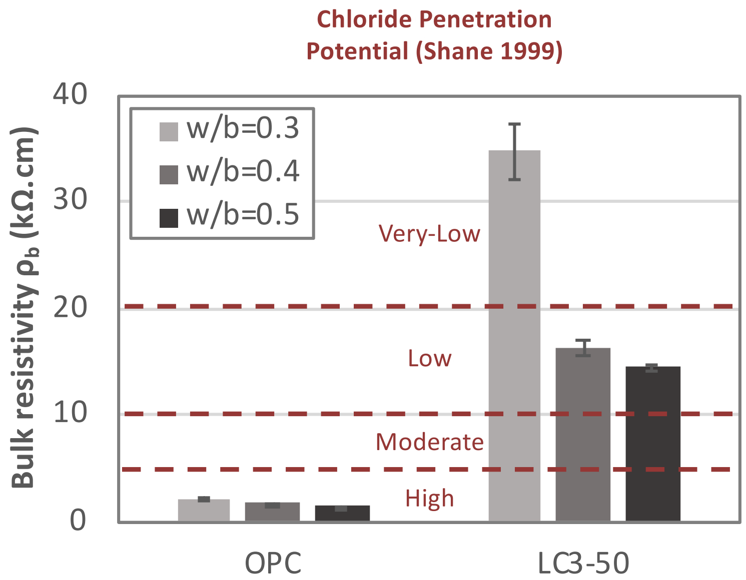
Chloride ingress in cementitious pastes
> Bulk resistivity as a rapid indicator

Porosity
Pore solution

- Very rapid indicator of chloride penetration potential (~7s)
  - Well correlated to standardized methods (e.g. RCPT)
  - Threshold values from Shane 1999

➢ Bulk resistivity is much higher for LC3-50

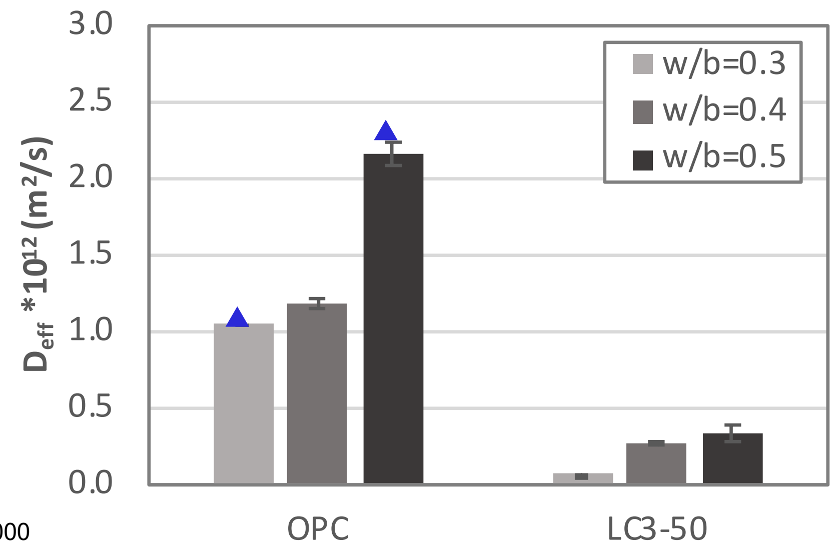




Chloride ingress in cementitious pastes
> Mini-migration tests

Porosity
Pore solution
Binding

- Results for OPC and LC3-50 systems
  - Results for OPC systems in agreement with previous results from Truc et al. 2000 ( )
  - Significantly lower diffusion coefficients for LC3-50 systems
  - Same trends as bulk resistivity results
    - Higher bulk resistivity → lower Cl- diffusion
    - Cl^- binding does not change the trend



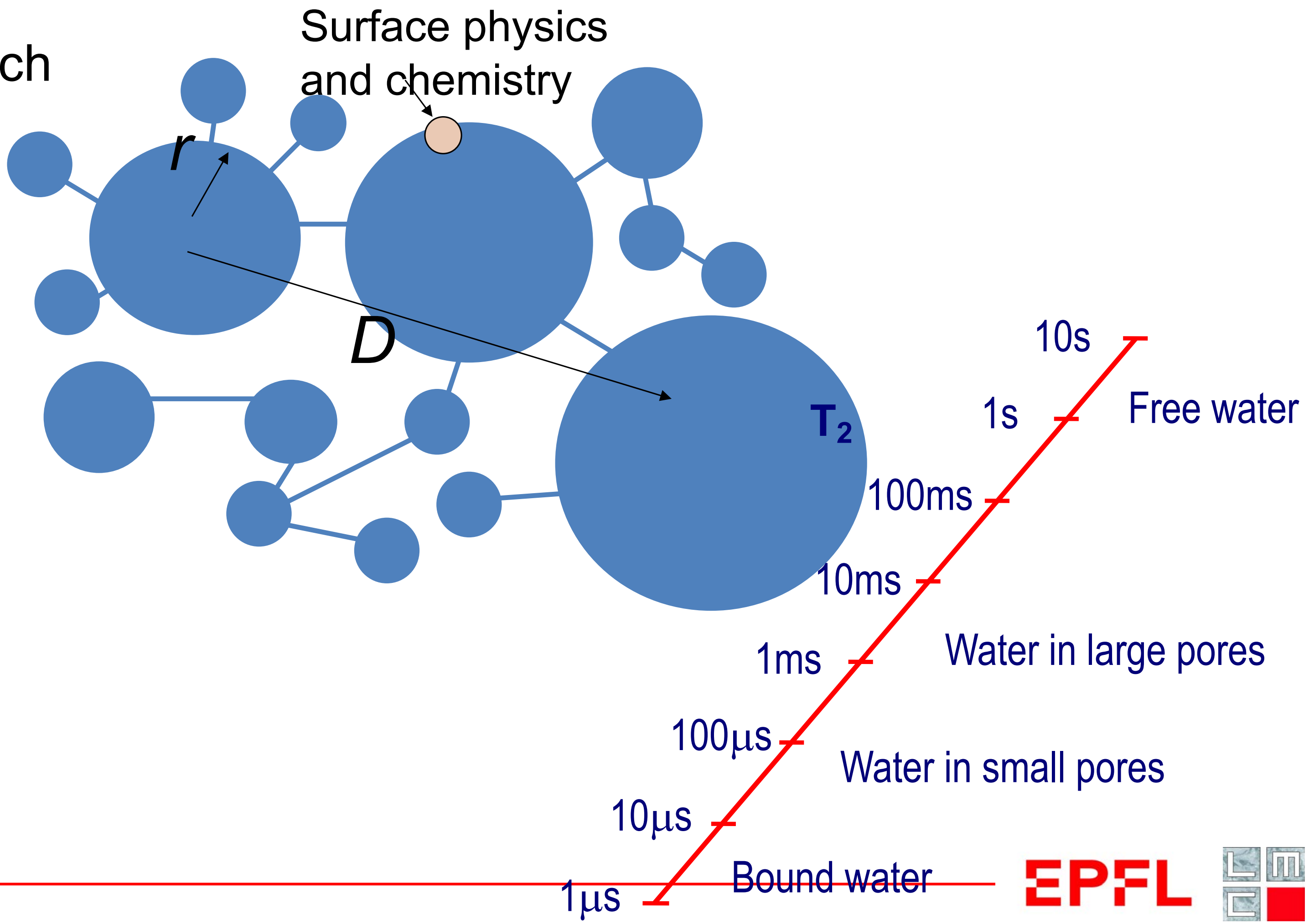
Truc et al., Cement and Concrete research 30, 2000

Links to microstructure
> Pore classes

- ^{1}H NMR analyses

Proton, ^{1}H Nuclear Magnetic Resonance

- a unique technique which can analyse porosity using water as a probe
- no drying is necessary
- in fact the pores must contain water to give a signal
- many, in-situ measurements on same sample



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Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Use of bench-top NMR to measure the density, composition and desorption isotherm of C–S–H in cement paste

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Desorption isotherm

ABSTRACT

^{1}H nuclear magnetic resonance (NMR), supported by a measure
ray diffraction, has been used to fully characterise the nano-sc
silicate–hydrate (C–S–H), the active component of cement. The
are $\rho = 2.68$ g/cm^3; $(Ca)_{1.53}\cdot(Si_{0.96}Al_{0.04})O_{3.51}\cdot(H_2O)_{1.92}$ for a
paste with an initial mix water-to-cement ratio of 0.4 after 2
pore-type resolved desorption isotherm of cement that shows
ative humidity has been measured. Critical to our results is veri
NMR spin–spin relaxation time components. These have been
The new methodology is key to enabling design of cement pas

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The morphology of C–S–H: Lessons from ^{1}H nuclear magnetic resonance relaxometry

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Nuclear magnetic resonance (NMR)

ABSTRACT

^{1}H nuclear magnetic resonance has been applied to cement pastes, and in particular
(C–S–H), for the characterisation of porosity and pore water interactions for over th
there is now renewed interest in the method, given that it has been show
non-destructive and fully quantitative. It is possible to make measurements of pore si
surface area, C–S–H density and water fraction and water dynamics over 6 orders of m
milli-seconds. This information comes in easily applied experiments that are increasin
widely available equipment. This contribution describes the basic experiments for a c
the field and reviews three decades of work. It concludes with a summary of the current
cement pore morphology from the perspective of ^{1}H NMR.

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Densification of C–S–H Measured by ^{1}H NMR Relaxometry

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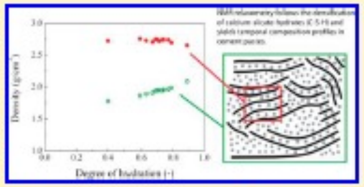
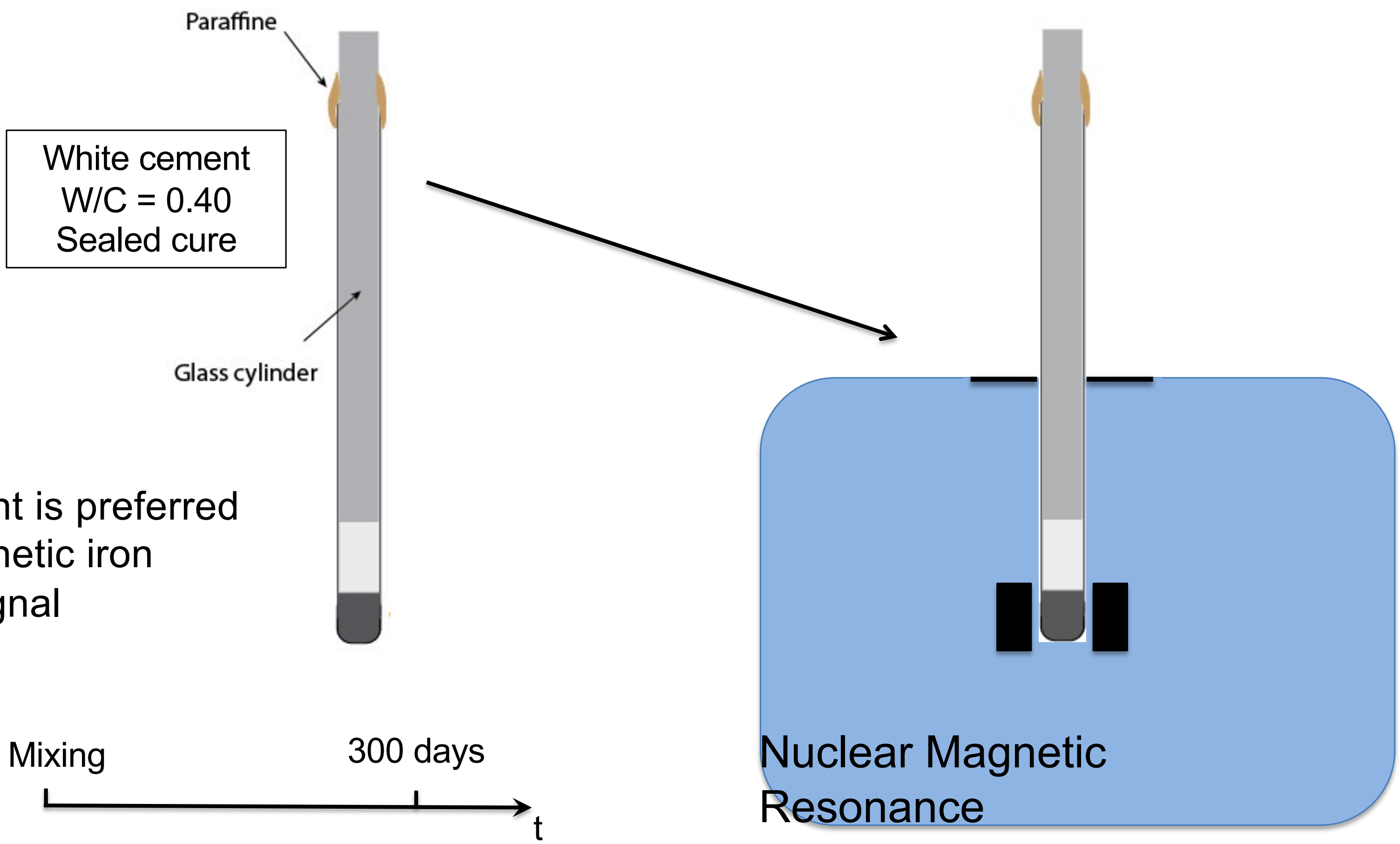
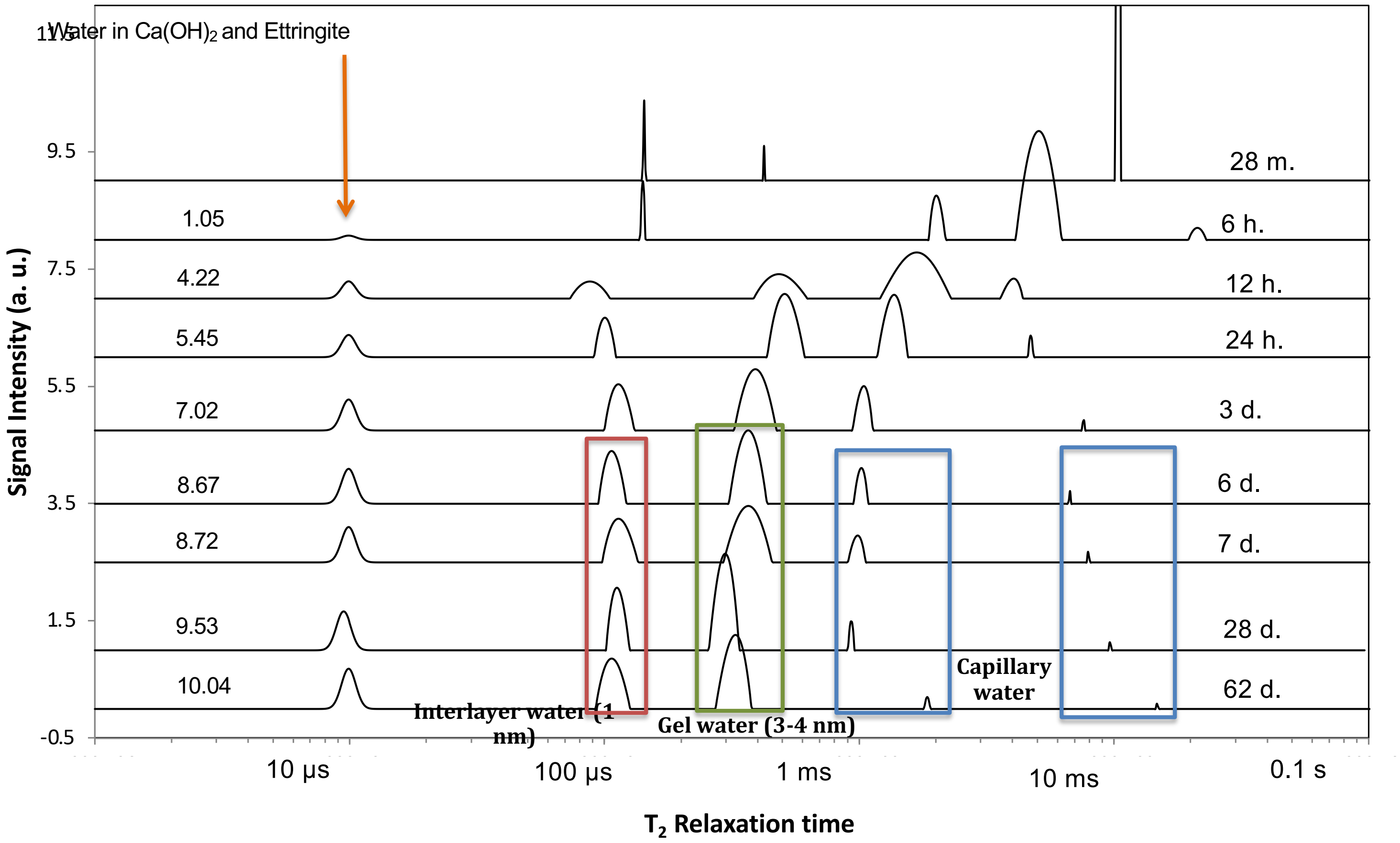


ABSTRACT: The nanoscale morphology of, and pore water interactions in, calcium silicate hydrate (C–S–H), the active component of cement, remain uncertain. ^{1}H nuclear magnetic resonance (NMR) can fully characterize the nanoporosity of C–S–H in as-prepared material without the need for damaging sample drying. We use NMR to follow the density of C–S–H in sealed cured pastes as a function of degree of hydration (α) and water to cement ratio. We show clear evidence for C–S–H densification. The C–S–H "solid" density, exclusive of gel pore water, slightly decreases from $\rho_s = 2.73$ g/cm^3 at $\alpha \approx 0.4$ to 2.65 g/cm^3 at $\alpha \approx 0.9$ due to an increase in the number of layers in the nanocrystalline aggregates. In the same range, the C–S–H "bulk" density, including gel water, increases from around 1.8 to 2.1 g/cm^3. The increase corresponds to a transition from growth of low-density product containing gel pores to higher density product devoid of gel pores. We update Powers' classical model from 1947. In contrast to the single "hydrate" of Powers, NMR differentiates between C–S–H and calcium hydroxide and separates out the interlayer water within the C–S–H. It shows a clear nonlinearity in the growth of the different fractions with α.

Experimental procedure

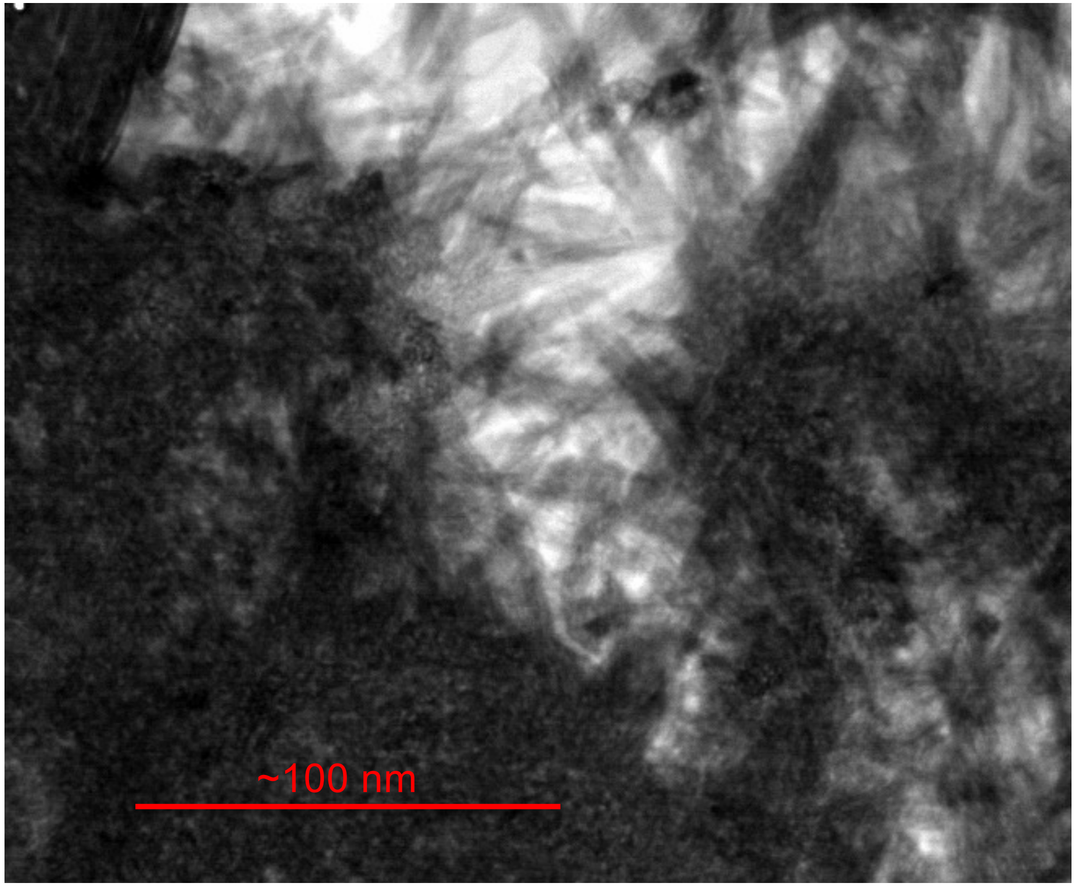


White cement is preferred as paramagnetic iron degrades signal



Water in Ca(OH)2 and Ettringite
11.5
9.5
7.5
5.5
3.5
1.5
-0.5
Signal Intensity (a. u.)
1.05
4.22
5.45
7.02
8.67
8.72
9.53
10.04
28 m.
6 h.
12 h.
24 h.
3 d.
6 d.
7 d.
28 d.
62 d.
Interlayer water (1 nm)
Gel water (3-4 nm)
Capillary water
10 µs
100 µs
1 ms
10 ms
0.1 s
T2 Relaxation time

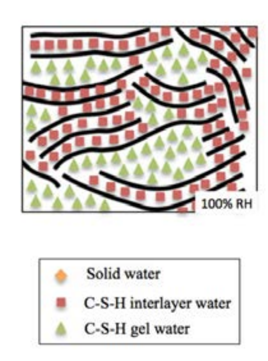
Interhydrate pores



Bazzoni 2014

Links to microstructure
> Pore classes

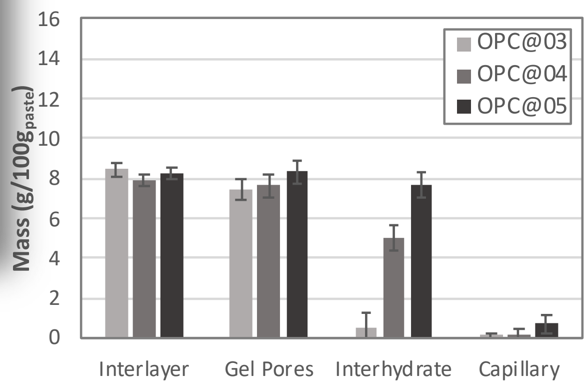
- ^{1}H NMR analyses
  - The method
  - Water families and pore size
  - Amount of each pore class

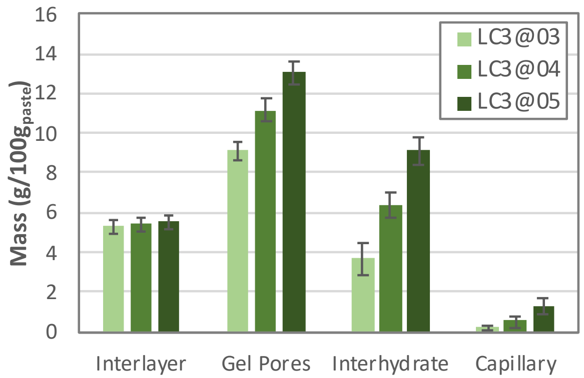


➢ Increasing w/b increases the amount of interhydrate + capillary water

➢ Which water is responsible for Cl$^-$ diffusion?

➢ The LC3-50 systems contains less C-S-H interlayer water, but more gel and interhydrate pores compared to OPC systems.



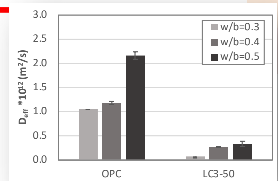


…not the reason for lower chloride diffusion in LC3…

Links to microstructure

> Tortuosity of the porous network

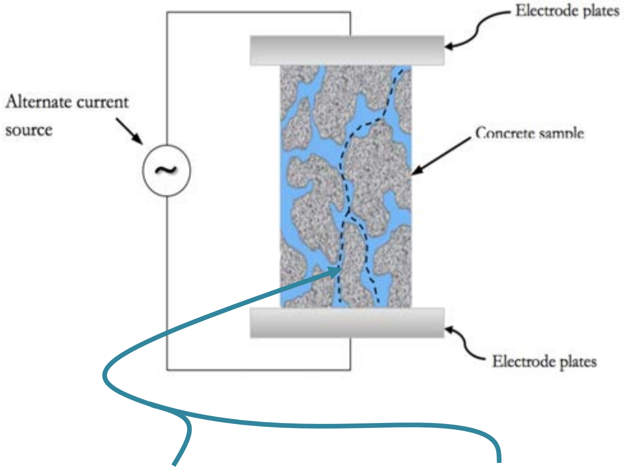
- Tortuosity from the formation factor



Porosity

Pore solution

$$F = \frac{\rho_b}{\rho_0} = \rho_b \sigma_0 = \frac{\tau_D}{\phi}$$



Porosity and tortuosity

Conductivity of the pore solution

ρ_b : Bulk resistivity (Ω.m)

ρ_0 : Pore solution resistivity (Ω.m)

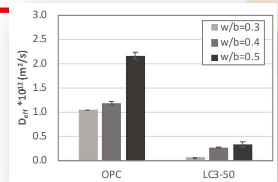
σ_0 : Pore solution conductivity ($\Omega^{-1}m^{-1}$)

F : Formation factor (-)

τ_D: Diffusion tortuosity (-)

ϕ : Porosity (-)

Links to microstructure
> Tortuosity of the porous network



Porosity

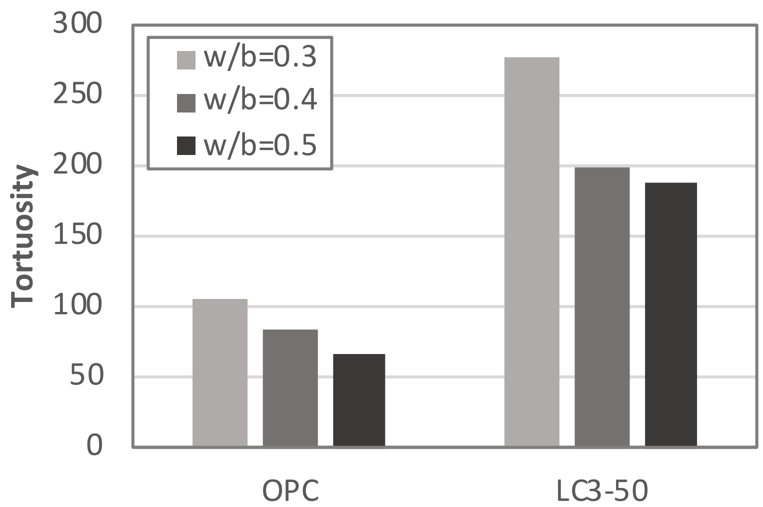
Pore solution

- Tortuosity from the formation factor
  - Results

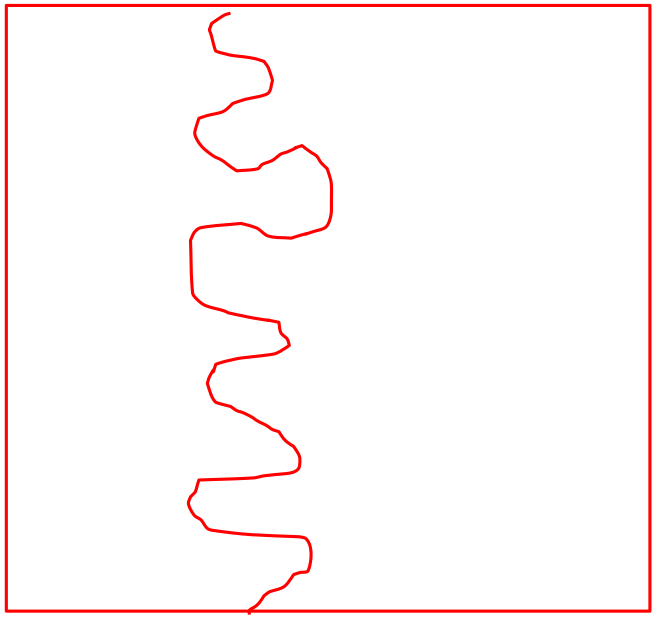
    - Although the amount of pores (gel+ interhydrate+capillary) is significantly higher for LC3-50 systems, the “tortuosity” of the porous network is 2-3 times higher than for OPC systems.

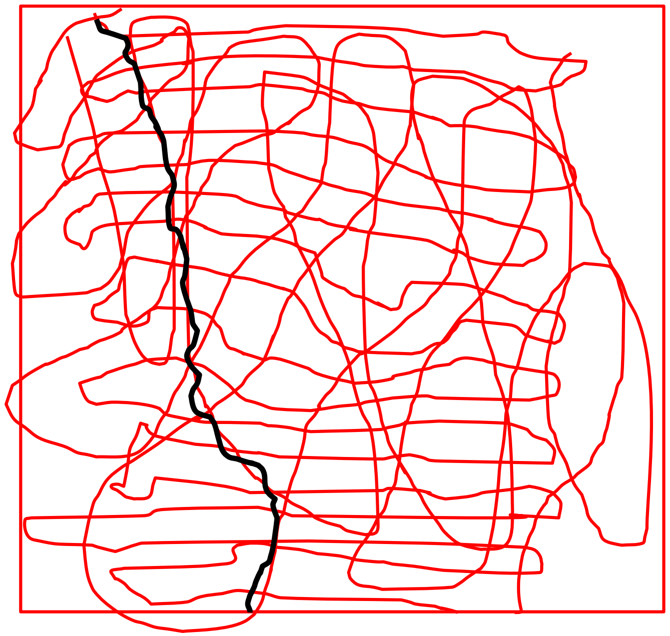
    - This tortuosity thus appear to be an important parameter affecting the diffusion coefficient.

    - **But these high values cannot be explained by simple geometry**



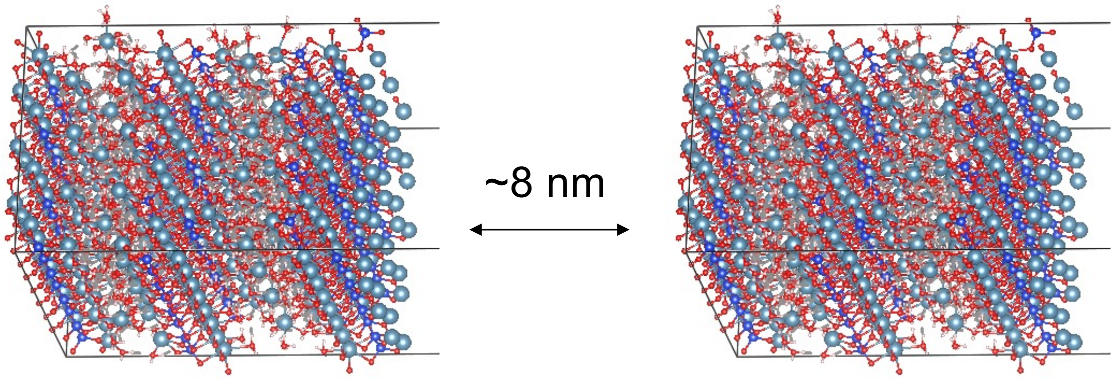
These tortuosity values not a result of geometry





Narrow pores, ionic gradients.

- Narrow channels dominate solution filled porosity
- Overlapping concentration gradients will dramatically affect Ion mobility

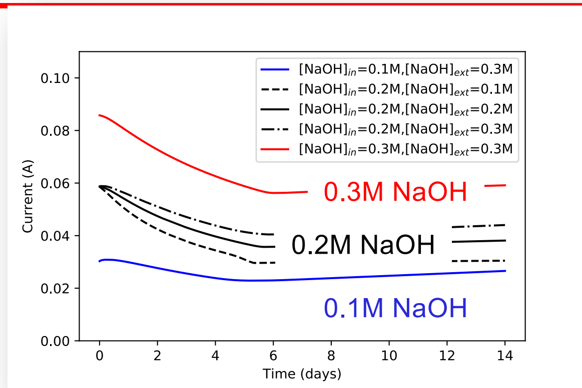


Links to microstructure
> *Pore solution composition*

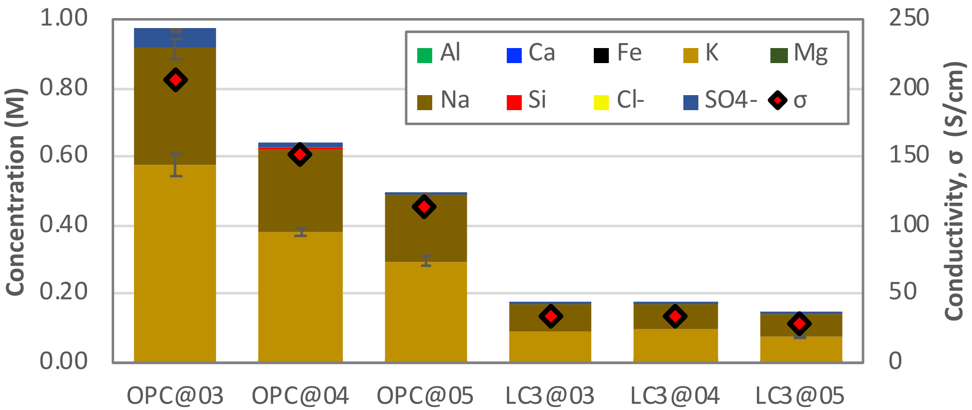
- Ionic concentration and conductivity
  - Characterization of the pore solution by ICP-EOS and IC

➢ The ionic concentrations of the pore solution of LC3 systems is much lower than that of OPC systems.

➢ *From simulation, the migration current and the chloride diffusion are function of the OH^- concentration in the pore solution.*



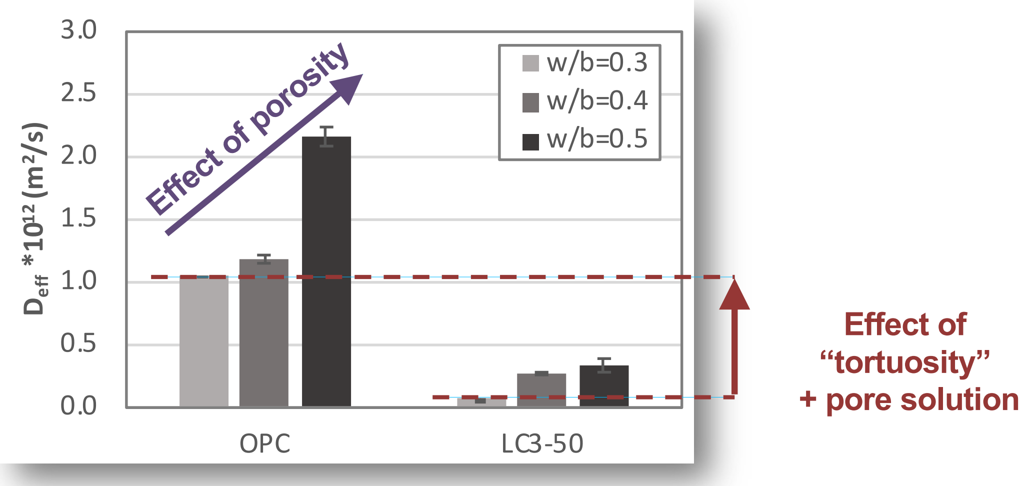
Georget, 2019



Links to microstructure

- Current understanding, for the investigated systems:

  > Diffusion coefficient vs. porosity vs. ionic concentrations



- However it is not clear is the origin of these "tortuosities"

Conclusions

- Need to optimise systems to reduce CO2 emissions
- Need to understand how different reactive ingredients contribute to space filling
- "Hierarchy" of reactivity:

  Alite > MK ~SF ~slag > flyash > belite
- Reduction of porosity roughly linear impact on strength
- For chloride ingress, other factors play a strong role:
  - Alkali ions in pore solution
  - Interaction of ions with surface of hydrates.

END

Thank you